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VAPOUR SORPTION STUDIES OF POLYMER-SOLUTION THERMODYNAMICS USING A PIEZOELECTRIC QUARTZ CRYSTAL MICROBALANCE

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ABSTRACT

A Quartz Crystal Microbalance, QCM, has been used as the basis of a vapour sorption apparatus to measure thermodynamic interaction parameters of polystyrene, poly(4-chloro styrene) and poly(methyl methacrylate) with a number of solvents. The apparatus has been shown to give rapid and reliable results by comparison with Literature results for PDMS. Measurements of activity coefficients and Flory-Huggins interaction parameters were correlated with the solution behaviour of the components and revealed some hitherto unreported effects of the solution concentration in polar systems.

Keywords: Quartz crystal microbalance; vapour sorption, PDMS, polystyrene, interaction parameters, polymer solution thermodynamics

1. INTRODUCTION

Knowledge of the thermodynamic properties of polymer – solvent mixtures is important in a number of areas ranging from the testing of solution theories to commercial applications such as the formulation of coatings as well as monomer or solvent removal during processing. A range of methods[1,2] is available for studying polymer solutions including the measurement of colligative properties such as osmotic pressure, solution viscometry, sedimentation, light scattering or neutron scattering methods. However, these are applicable in the main to dilute solutions of polymer. For a number of applications such as coatings, paints, inks, membrane separations or polymer processing, the main interest is where the solvent is present in low quantities. Measurements on concentrated solutions are therefore needed. Here, the choice of methods is more limited and inverse gas chromatography[3] and vapour sorption[4] are the usual methods. The latter consists of determining the equilibrium mass of solvent isothermally absorbed by a known mass of polymer when exposed to a certain vapour pressure of solvent. Mass detection can be by the change of length of a quartz spring[5], a sensitive electronic microbalance[6] or, more recently, by a piezoelectric sorption detector. This detector, also known as the *Quartz Crystal Microbalance, QCM*, monitors the frequency change of an oscillating quartz crystal. Sauerbrey[7] showed that, within certain limits, the frequency change ΔF varies linearly with a change in applied mass, Δm, according to Equation (1).

$$\Delta F = \left(\frac{F_o^2}{AN\rho_q} \right) \Delta m \qquad (1)$$

where F_o is the fundamental oscillation frequency of the quartz crystal, A is the active area of the gold, N is a constant for the particular grade of quartz related to its shear modulus and ρ_q is the density of quartz. Calculations show that the ultimate sensitivity of this type of detector is in the region of nanograms of material although operational considerations usually limit this to 0.01 – 0.1 μg.

While it is well known that Equation (1) is at best an approximation, it is adequate so long as the frequency change is limited to < 0.02 F_o and the fluid in which the crystal operates causes low acoustic loss. Greater absolute accuracy can be achieved by measuring the impedance changes across the crystal rather than the simple frequency change[8] but for straightforward work, particularly where the system may readily be calibrated, the Sauerbrey equation is satisfactory. This has been shown to be the case for solutions of the type studied here[9].

QCM's are well established in the field of thin film monitoring[10] and have been used as chemical sensors[11] monitoring the absorption of gases and vapours by crystals covered with functionalised coatings. A major advantage of the piezoelectric sorption detector is that, in addition to being rapid, it uses small amounts of polymer spread in a thin film under circumstances similar to those adopted in practice.

Bonner and Chang[12] showed that this type of apparatus could be used to study nitrogen sorption by low density polyethylene at 125°C and pressures up to 2000 psi. The sorption of organic vapours by polystyrene has been studied by Saeki and co-workers[13] who found that precise values of activity coefficients could be attained with short equilibration times in the order of 10 min. Wong and co-workers[14] applied this technique to the sorption of three solvents by polystyrene and found that accurate results could be obtained rapidly. Activity coefficients of solvents in a series of elastomeric polymers were measured by French and Koplos[15] who found reasonable agreement with some literature systems.

The work described here is part of a programme aimed at studying the effect of solvents on thin films of polymers such as those used for photoresist and masking materials. Examples include polystyrene, PS, poly(4-chlorostyrene), PClS and poly(methyl methacrylate), PMMA. Organic polymers have largely been superceeded for the production of very large scale integrated (VLSI) circuits but are still in use for many other applications.

Likewise, there is a move away from organic solvents to minimise environmental impact nut organic systems are more straightforward and give a good basis on which to develop methodology. Interactions with polymer films are controlled by kinetic factors as well as thermodynamic polymer/solvent interactions. The interactions between the polymer and solvent molecules give an indication of thermodynamic compatibility.

To enable a correlation between observed dissolution kinetics and thermodynamic interaction, the activity coefficients and interaction parameters have been measured for a series of polymer/solvent systems close to those used in our dissolution studies[16].

2. EXPERIMENTAL

2.1 The apparatus

A schematic diagram of the apparatus is shown in Figure 1. The quartz crystal was mounted in an accurately thermostatted chamber which could be evacuated and filled with solvent vapour at precisely controlled pressures.

Figure 1 near here

Basic pumping was provided by means of an Edwards rotary vacuum pump and this was backed with a mercury diffusion pump with a liquid nitrogen trap. The pressure in the pumping line was monitored using Edwards "Pirani" and "Penning" meters. The sorption apparatus was designed for operation from 1×10^{-5} Torr up to atmospheric. The pressure in the sorption chamber was measured with a precision of ± 0.01 torr using a M.K.S. Instruments "Baratron" 270 capacitance pressure gauge operated with a 1000 Torr head. The gauge was connected to the sorption vessel by means of a glass line which was maintained at a temperature greater than the sorption vessel by means of heating tape to prevent condensation of solvent vapour. All taps which could come into contact with solvent were PTFE to prevent interaction of solvent vapours with grease.

A commercially available Edwards FTM5 thin film monitor was used to monitor the frequency of the quartz crystal. This QCM set-up allowed monitoring of the crystal frequency with a resolution of ± 0.1 Hz. AT cut, 6 MHz quartz crystals (diameter 14 mm, electrode diameter 7 mm, thickness 0.5 mm) were supplied by Edwards. The crystal was supported by a holder through which thermostatted water was circulated. The holder was mounted in a glass flange which was bolted to the absorption chamber by means of a coupling incorporating a copper gasket so that no rubber 'O-rings' were in contact with solvent vapour.

Thermostatting to ± 0.01°C was achieved by circulating water from a Grant W14 circulating water bath. The sorption vessel was also enclosed in a box containing a heating fan to further control the temperature to ± 0.1°C. The vessel temperature was monitored by a mercury in glass thermometer calibrated against a Tinsley Type 5840 platinum resistance thermometer.

2.2 Procedures

Prior to coating with polymer, the frequency, F_o, of the uncoated crystal was recorded. Coating was accomplished by spin coating a few drops of ~ 0.5 wt% polymer solution onto the top face of the crystal. After evaporation of the solvent, the oscillation frequency was re-measured to give the frequency change corresponding to the polymer layer, ΔF_p. Polymer film thicknesses of 0.2 – 2.0 μm were obtained, corresponding to 0.05 – 0.2 mg of material.

The crystal was placed in the sorption vessel, and the unit sealed. It was then evacuated to < 0.001 torr and this pressure maintained for at least 8 hr until a stable frequency was obtained. Before commencing each experiment, the leak rate of the system was measured to ensure that any leak of air into the system would be negligible in comparison with the solvent pressure. Prior to each run, the solvent to be used was degassed by at least three successive freeze-thaw cycles.

To begin the measurement of an absorption isotherm, the evacuated chamber was isolated from the pumps and a small amount of solvent vapour (~5 - 20 torr) was admitted. The frequency change due to absorption of the solvent by the polymer was monitored by the FTM5 until equilibrium had been reached, indicated by constant values of pressure and frequency. Further solvent vapour was admitted and the procedure repeated to record the isotherm.

2.3 Materials

The poly(dimethyl siloxane), PDMS, sample was a DC 200 silicone fluid with viscosity 1000 cs obtained from Dow Corning Ltd. The number average (M_n) molecular weight was measured by GPC as 26000. The polystyrene, PS, was a secondary standard with a M_W of 430000 and polydispersity, $\gamma = 2.1$ obtained from the Aldrich Chemical Company. Poly(4-chlorostyrene), P4ClS, was prepared by radical polymerisation using a 0.1 wt% azobisisobutyronitrile initiator in a 50% solution of inhibitor free 4-chlorostyrene (Aldrich Chemical Company) in toluene. It had $M_n = 60000$ and $\gamma = 1.88$ as measured by Gel Permeation Chromatography relative to polystyrene calibration standards. The PMMA used was supplied by BDH Ltd produced by radical polymerisation. It had $M_n = 56000$ and $\gamma = 2.0$ as measured by GPC.

The solvents used as absorbates were of the purest grade available: BDH ‘Research Grade’ for benzene, hexane, cyclohexane while chloroform, 2-butanone (methyl ethyl ketone, MEK) and propan-2-ol (isopropyl alcohol, IPA) were ‘Analar’ (99.5+%)grade from BDH. Methyl, ethyl, *n*-propyl and *n*-butyl acetates were the purest grade from Aldrich and were distilled over potassium carbonate prior to use. Methanol was distilled from calcium hydride. Prior to use, the solvents were distilled between glass flasks attached to the vacuum frame in order to purify and degas the solvent.

2.4 Solvent Sorption on an Uncoated Crystal

To account for any effect of pressure on the response of the bare crystal which might lead to errors in the mass measurements, Figure 2 shows the frequency change, ΔF, when an uncoated crystal was subjected to varying pressures of hexane or air at 30 °C. An air pressure of 400 torr produced a frequency change of 35 Hz, a linear relationship being found between change in frequency and pressure. The larger change in ΔF for hexane than in air is related to the difference in vapour density.

Figure 2 near here

The results indicate the importance of maintaining a leak-free system if accurate pressure measurements are to be made. In addition, the response of a blank (uncoated) crystal to each new vapour studied was recorded and subtracted from the mass absorbed by a polymer coating. This procedure is the equivalent of a bouyancy correction in a conventional gravimetric experiment.

3. RESULTS AND DISCUSSION

Activity coefficients and Flory-Huggins interaction parameters were calculated from the vapour sorption data in the following manner. Using Sauerbrey's Equation (1), the weight fraction of solvent, w_1, sorbed by the polymer can be calculated using:

$$w_1 = \left(\frac{m_1}{m_1 + m_p} \right) = \left(\frac{\Delta F_1}{\Delta F_1 + \Delta F_p} \right) \tag{2}$$

where ΔF_1 is the frequency change due to the mass of solvent, m_1, absorbed by the polymer on the crystal and ΔF_p is the frequency change due to the polymer coating of mass, m_p. The volume fraction of solvent, φ_1, can be calculated from:

$$\varphi_1 = \left(\frac{(\Delta F_1 / \rho_1)}{(\Delta F_1 / \rho_1) + (\Delta F_p / \rho_p)} \right) \tag{3}$$

where ρ_1 is the density of the liquid solvent and ρ_p that of the polymer. Note that the use of Equations (3) and (4) does not require that the system precisely follows Sauerbrey behaviour, merely that there is a linear relationship between mass and frequency change.

At equilibrium, the volume fraction activity coefficient ${}^v\gamma_1$ of the solvent at a given solution temperature is given by[17, 18]

$$\ln {}^v\gamma_1 = \ln\left(\frac{P_1}{P_1^\circ \varphi_1}\right) + \frac{\left(V_1^\circ - B_{11}\right)\left(P_1^\circ - P_1\right)}{RT} + 0.5\left(\frac{B_{11}}{RT}\right)^2\left(P_1^{\circ 2} - P_1^2\right) \quad (4)$$

where P_1 is the partial pressure of solvent above the polymer solution, P_1° is the saturated vapour pressure of solvent at the solution temperature T, B_{11} is the second virial coefficient of the solvent, V_1° is the molar volume of solvent and R is the gas constant. Pure component data were taken from reliable Literature sources[19,20]. The activity coefficient in Equation (4) is calculated on a volume fraction basis rather than the more familiar mole fraction basis since the latter is dependent on precise values of the polymer molecular weight. In addition, the latter does not give physically reasonable description of polymer solution behaviour[21]. From ${}^v\gamma_1$, the Flory-Huggins interaction parameter, χ, may be obtained.

$$\ln {}^v\gamma_1 = \ln \varphi_1 + \left(1 - \frac{1}{r}\right)\varphi_p + \varphi_p{}^2 \chi \quad (5)$$

In the original Flory-Huggins formulation, χ, was a concentration and molecular weight independent parameter that accounted for enthalpic differences on mixing between the polymer and solvent. However, it is now widely recognised that χ does vary with these parameters and is often represented as varying linearly with volume fraction, although more complex behaviour has been observed in some systems[22].

$$\chi = \chi_o + \chi' \varphi_1 \quad (6)$$

The dependence of χ on molecular weight is less clear but has been observed in a number of systems[1,23,24], the main influence being at low chain lengths. χ is more correctly interpreted

as a partial molar residual Gibbs free energy of mixing (the "non-combinatorial" free energy) for the polymer and solvent, that is the Gibbs free energy of mixing that is not accounted for by mixing of the polymer segments and solvent molecules on a lattice, and so contains enthalpic (χ_H) and entropic (χ_S) contributions.

$$\chi = \left(\frac{\Delta \overline{G_1}^R}{\varphi_2^2 RT} \right) = \chi_H + \chi_S \tag{7}$$

There are a number of theoretical descriptions to describe and account for χ with varying levels of complexity[1]. However, in order to provide a framework for describing solution behaviour in our systems, it is sufficient to use χ as an empirical parameter describing solvent "quality". Low values of χ indicate favourable mixing between the polymer segments and solvent while higher values indicate increasingly unfavourable interactions and poor solvent behaviour.

3.1 PDMS/Solvent Systems

Before commencing study of novel systems, it was important to demonstrate that our apparatus was capable of producing results with the desired accuracy. Absorption isotherms were recorded for benzene, hexane, and chloroform in PDMS. These systems have been amongst the most studied and Literature results give a good basis for comparison.

Absorption isotherms were recorded and volume fraction activity coefficients and Flory-Huggins interaction parameters calculated. Figure 3 shows an example isotherm for hexane in PDMS at 30 °C. The change in frequency for an uncoated crystal is much smaller than when coated with PDMS. Activity coefficients agreed with Literature values [6, 18, 21, 25, 26] to within an average of ± 1.5% for the solvent systems studied. This is within the experimental uncertainty of the method. A more stringent comparison can be made with the χ parameters which are much more susceptible to uncertainty in experimental measurements. For most systems, the contribution to the overall solvent activity from the interactions is small

since the activity of the solvent, a_1, is dominated by entropic effects. Changes in χ therefore form only a small part of variation in activity coefficients. The χ values calculated from this work are shown in Figure 4 along with Literature values[6] recorded on a comparable material.

Figure 3 and Figure 4 near here

Agreement between data becomes less satisfactory at very low concentrations as the uncertainties in the measurements are more significant in this region. For $\varphi_1 < 0.05$, an error in the measured frequency change of ± 0.1 Hz, could cause a deviation of the calculated activity coefficient of ± 2%, and an error as great as ± 10% in χ. At higher concentrations, the uncertainties will be lower; for a typical system at $\varphi_1 \sim 0.3$, a 0.1 Hz change could cause an uncertainty of 2 - 5% in χ. In comparison, the uncertainty in the mass of the polymer coating is negligible. The Literature results[6] have previously been shown to give good agreement with those of other workers and methods. Thus, we are confident that our apparatus gives accurate and meaningful data.

3.2 Polystyrene/Solvent Systems

In contrast to PDMS which is liquid at ambient temperatures, polystyrene is a glassy solid so that it was again important to demonstrate that the procedures yielded accurate results with this type of system. The rigid nature of the PS film introduces an additional factor that needs to be considered. On absorption of solvent, the viscoelastic properties of the coating will change as solvent is absorbed. This may induce a frequency shift in the crystal[27] irrespective of any mass change leading to a potentially erroneous application of Equation (2). Results from a number of studies of PS solutions have been published so that again there is a good basis for comparison.

Measurements for a range of solvents in PS were made. Our results for the solvent activity and activity coefficients correlate well with previously published literature results[1, 13,

[14] for benzene, chloroform and cyclohexane. As noted above, the determination of χ is a more stringent test of the method. Values for the sorption of benzene and chloroform on PS was measured at 25, 30 and 35 °C and are shown in Figure 5. Results at 25 °C were recorded with two quartz crystals coated with different polymer film thicknesses (ΔF_o = 1712 and 1990 Hz) but they fall on the same line, demonstrating the reproducibility of our results.

Figure 5 near here

Also shown by the solid lines in Figure 5 are the results of Wong et al.[14] which were shown to agree reasonably well with previously published data[13, 28]. The measurements from which the lines were derived would have carried the same order of uncertainty as the results reported here so that when the error bars are taken into account, good agreement is seen between the results, particularly at low concentrations. It was noticeable that there is much less scatter in the results recorded using QCM's than with gravimetric microbalances. This is in part due to the difficulty of establishing equilibrium when using the relatively large amounts of polymer needed for accurate gravimetry. The QCM experiments are much quicker to conduct. Establishment of equilibrium conditions took in the region of 45 – 90 min for the early points where diffusion into the glassy matrix was slow but this reduced to 10 – 15 min for the later points. A complete isotherm could therefore be measured over the course of several hours, in contrast to the several days that can be necessary with other methods[5].

The temperature dependence of the solvent absorption shows that the interaction parameters decrease with rising temperature indicating a positive enthalpy of mixing. This indicates that the solvents become progressively better so that polymer-solvent interactions become more favourable. The temperature dependence of χ is generally represented as

$$\chi = a - \frac{b}{T} \qquad (7)$$

To investigate this, the results in Figure 5 were extrapolated using the linear relationship of Equation (6) to zero solvent concentration to give 'infinite dilution' interaction parameters, χ^{∞}. The values for benzene and chloroform are plotted in Figure 6 and show satisfactory fit to Equation (7). In principle, such plots could be used could be used to calculate the enthalpy of mixing for the polymer and solvent (related to *b* in Equation (7)). However, the experimental uncertainty in the measurements is too high to yield meaningful results.

Figure 6 near here

Having established the precision and reproducibility of our methods, we turned to previously unpublished systems that were of interest in our related work on radiation induced solubility changes. Figure 7 shows that relatively high χ values were obtained for hexane, cyclohexane, 2-butanone and 2-propanol characteristic of them being poor solvents for PS. The similarity of results for n-hexane and cyclohexane suggests that entropic considerations are relatively unimportant in these systems since enthalpic mixing will be the same. The results can be compared with values reported in the correlation by Hansen[32] of $\chi = 1.0$ at 40 °C for hexane measured at infinite dilution (i.e. $\varphi_p = 1$) by inverse gas chromatography and for 2-butanone $\chi = 0.8 – 0.9$ at 25 °C for $\varphi_p = 0.8$ - 1.

Figure 7 near here

The concentration dependence of χ for the alkanes and 2-butanone is small. In contrast, the variation with 2-propanol is markedly different. There is a steep increase of χ with concentration at low volume fractions ($\phi < 0.05$) before it passes through a maximum. The dependence is much larger than in the other systems. The explanation for this behaviour is unclear. It has often been observed[29] that χ decreases with rising solvent concentration, particularly for poor solvents while there is little variation in good solvents except where strong polymer solvent interactions occur. This is the case for hexane, cyclohexane, 2-

butanone but it is difficult to see how strong polymer-solvent interactions could occur with PS/2-propanol to give the observed sharp rise in χ.

One possibility might be that 2-propanol is such a poor solvent that the system did not reach equilibrium in a glassy matrix. However the results were reproducible, showed no dependence on polymer film thickness and there was no noticeable hysteresis when results were measured while decreasing the vapour pressure of solvent. In addition, calculations show that if the system had not attained equilibrium then values of γ and χ would have been overestimated rather than starting low and increasing. Thus, we are confident that the results are not an artefact of our measurement technique.

The previously observed non-linear variation of χ with φ has been explained by the varying contributions to the residual Gibbs free energy and the way that they change with concentration. The enthalpic contributions arise from exchange of contact interactions while the non-combinatorial entropy mainly arises from the reduction of free volume as the solvent penetrates the polymer and to the change in chain conformations that arise due to relaxation.

In the case of PS/2-propanol, the enthalpic contribution would be highly unfavourable due to the different chemical nature of the two components. Relatively few exchange contacts would be formed at low concentration of 2-propanol. This would also mean relatively small changes to the free volume until the concentration is high enough to fill most of the free volume in the glassy film. At this point, larger entropy changes would occur leading to the fall in χ. An extension of this model might be that low concentrations may not penetrate the whole of the film but our current measurements do not allow further speculation on these points.

3.3 Poly(4-chlorostyrene)/Solvent Systems

P4ClS has been used as a photo- and e-beam resist material, the halogen substitution leading to enhanced radiation sensitivity. Addition of the chlorine atom to PS also makes the polymer somewhat more polar and so differences in the interaction parameters might be expected.

The interaction parameters for the sorption of four solvents studied at 30°C are shown in Figure 8.

Figure 8 near here

Benzene and cyclohexane are good and poor solvents for P4ClS respectively and this is shown by their χ values as well as the concentration dependences which, while small, are in opposite directions. An indication of the uncertainty in the measurements is given in Figure 8 and the small rise in χ at very low concentrations is insignificant. The uncertainties in the measurements and hence the scatter of experimental data is relatively high at these lowest concentrations. The values for benzene and 2-butanone are somewhat lower than those previously reported[33] although it should be noted that those measurements were on poly(2-chlorostyrene) at 25 °C. The values for cyclohexane in P4ClS are similar to those for PS indicating a similar degree of interaction in a system that can only interact *via* van der Waals type intermolecular forces. Those for benzene are lower than PS showing that the increase in polarity enhances the interactions. There is also a higher concentration dependence than with PS. These effects are attributable to the more polar nature of the polymer segments and, presumably, the higher polarisability of the aromatic solvent. This would tend to make the χ_H contribution to χ more favourable. In addition, the polarity would invalidate the assumption of pseudo-random mixing on the lattice implied by the first two terms of Equation (5) so that an additional entropic contribution would also be expected over and above those in non-polar systems.

Mixtures of 2-butanone and 2-propanol are used in processing polymer films, variation of the proportions of each being used to control the exact solvency properties. The contrast in the behaviour of these two solvents can also be seen in Figure 8.

For the sorption of 2-butanone, χ is small and increases to a small extent with concentration correlating with the good solvent behaviour whereas the values for 2-propanol are very high. The interaction parameter is almost independent of solvent concentration, with an average value of 1.9 indicating the very small interaction between solvent and polymer. 2-propanol is a non solvent and presumably the highly polar and hydrogen bonded nature of 2-propanol is sufficient to outweigh interactions with the polymer. However, it is noticeable that the very steep concentration dependence seen with PS is not shown here. Further comparison of the corresponding values with PS and P4ClS shows that 2-butanone is a better solvent for the latter material, consistent the idea of better polymer-solvent interaction promoted by the polarity.

3.4 PMMA/Solvent Systems

In view of the widespread use of PMMA, there is a surprising dearth of information available on its solution thermodynamics[1, 29, 34]. As with P4ClS, mixtures of 2-butanone and 2-propanol are used in industrial coating and developing systems. Alternatives are n-alkyl acetates. These solvent systems were therefore studied along with some more straightforward solvents which will assist with interpretation of results.

Figure 9 shows the interaction parameters for hexane and benzene at 30 °C and 40°C. As with PS, benzene is a better solvent than hexane (which is a non solvent) and that the interaction is enhanced at lower temperatures. The deviation from linearity at 30°C may be due to the increased uncertainty in the results arising from the longer equilibration times required at the lower temperature. There is an insignificant temperature dependence for the

hexane results, again consistent with the negligible polymer-solvent interactions implied by the high value of χ.

Figure 9 near here

The interaction parameters for the sorption on 2-Butanone and three alcohols are shown in Figure 10. Again, the distinction in behaviour is clear. For butanone, χ indicates favourable interactions at low solvent compositions which become less favourable as the concentration rises and there was no significant variation between the two temperatures. Presumably, polar interactions between the ketone and the polar ester groups are responsible for the favourable sorption but these become saturated at low volume fractions of solvent.

Figure 10 near here

Each of the alcohols is a non-solvent for PMMA and this is reflected in the high χ values. The behaviour of methanol and ethanol mirrors that of 2-propanol on polystyrene with an initial sharp rise in χ before it levels off. As noted above, this may be due to the highly polar nature of these solvents precluding significant formation of polymer-solvent contacts. 2-propanol is the least polar of the three and shows a lower concentration dependence. It may also be able to interact more effectively with the ester group in PMMA than the non-polar PS. The maximum value of χ is the same for all three alcohols but is reached at a lower volume fraction of methanol. This may reflect the density difference between the alcohols; there will be a larger number of moles of methanol than in the same volume fraction of ethanol so that any polar interactions will be saturated at a lower concentration. It may also reflect the smaller size of methanol which can more readily diffuse into the glassy polymer. It is known that sorption of methanol has a plasticizing effect on PMMA so that free volume effects may become observable at lower concentrations.

Measurements of activity coefficients and interaction parameters for the n-alkyl acetates were carried out and the variation of χ with solvent volume fraction is shown in

Figure 11. A regular variation with the alkyl chain length might be expected but this was not observed. The χ values for the first three members of the series were very similar and again displayed the irregular increase with volume fraction that has been observed with other polar systems. When the chain length increases to a n-butyl substituent, χ increases markedly showing that it is significantly less compatible with PMMA. It may be that the C_4 alkyl chain overcomes any interaction between the polar ester groups. The reverse is the case for the shorter alkyl groups where the order of χ follows the molecular size although the variation is very small.

Figure 11 near here

4. CONCLUSIONS

The results reported here further confirm the utility of using QCM apparatus for the measurement of thermodynamic properties of polymer solutions and widens its applicability to highly polar systems. The results produced were satisfactory in terms of their precision and agreement with previously published work although improvements in sensitivity could be made by, for example, using crystals with a frequency higher than the 6 MHz used here. This type of apparatus has advantages over more traditional vapour sorption methods in that only small amounts of polymer are needed for accurate results and it is spread in a thin film, analogous to the circumstances in which polymer films would occur in applications. The relatively thin films also mean that measurements can be made more quickly. Although not exploited here, a very wide range of conditions such as temperature and pressure can be used[34].

The main aim of this work was to report interaction parameters which are relevant to a number of commercial polymer-solvent systems. In looking at new combinations, some unusual concentration dependences of χ have been observed. While these can be explained

qualitatively by considering the various enthalpic and entropic contributions to χ and seem to correlate with the polarity *difference* between polymer and solvent, more work is needed before a satisfactorily quantitative model of these systems can be confirmed.

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DEDICATION

I was introduced to the world of polymer photochemistry and photophysics by Ian Soutar who was spending research leave at the University of Toronto when I arrived as a postdoctoral fellow. The work reported here arose later from this beginning. Ian remained a much respected colleague – and friend – ever since. His unerring good humour and common sense will be sadly missed.

REFERENCES

1. R.P. Danner and M.S. High *Handbook of polymer solution thermodynamics* A.I.Ch.E., New York, 1993
2. H. Fujita *Polymer Solutions* Elsevier, Amsterdam 1990
3. *Inverse Gas Chromatography: Characterisation of Polymers and Other Materials*; Lloyd, D. R.; Ward, T. C.; Schreiber, H. P., Eds.; Amer. Chem. Soc.: Washington DC, 1989; Vol. 391.
4. C. Wohlfarth *Vapour Liquid Equilibrium data of binary polymer solutions* Elsevier, Amsterdam 1994
5. J.G. Lieu and J.M. Prausnitz, *Polymer* **40**, 5865 (1999)
6. A.J. Ashworth and G.J. Price, *Thermochimica Acta* **82**, 161 (1984)
7. G. Sauerbrey, *Z. Phys.,* **155,** 206 (1955)
8. A.L. Kipling and M. Thompson, *Anal. Chem.,* **62,** 1514 (1990)
9. J.W. Grate, S.N. Kaganove, V.R. Bhethanabotla, *Faraday Discuss.,* **107,** 259 (1997)
10. A. Wajid, *Sensors and Actuators A-Physical* **63,** 41 (1997)
11. S. Zhang, Z.K. Chen, G.W. Bao, S.F.Y. Li, *Talanta* **45,** 727 (1998)
12. D.C. Bonner and Y.L. Chang *J. Polym. Sci. Polym. Lett. Ed.* **13,** 259 (1975)
13. S. Saeki, J.C. Holste and D.C. Bonner, *J. Polym. Sci. Polym. Phys. Ed.* **20**, 805 (1982)
14. H.C. Wong, S.W. Campbell and V.R. Bhethanabotla, *Fluid Phase Equilibria* **139,** 371 (1997)
15. R.N. French and G.J. Koplos, *Fluid Phase Equilibria* **158,** 879 (1999)
16. G.J. Price and J.M. Buley, *Prog. Org. Coatings*, **19(3)**, 265-274, (1991).
17. D.C. Bonner and J.M. Prausnitz, *J. Polym. Sci., Polym. Phys.* **12**, 51 (1974)
18. P.J. Flory and H. Shih, *Macromolecules* **5**, 761 (1972)
19. *Selected values of the properties of hydrocarbons and related compounds:* Thermodynamics Research Centre Data Project, College Station, Texas, 1965 and later revisions.
20. J.H. Dymond and E.B. Smith, *The virial coefficients of pure gases and mixtures, a critical compilation* Clarendon Press, Oxford, 1980.
21. D. Patterson, Y.B. Tewari, H.P. Schreiber and J.E. Guillet, *Macromolecules*, **4**, 356, (1971)
22. H.M. Petri, N. Schuld and B.A. Wolf *Macromolecules* **28**, 4975 (1995)

23. A.J. Ashworth and G.J. Price, *Macromolecules* **19**, 358 (1986)
24. A.F.M. Barton *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters* CRC Press, Boca Raton 1990
25. G.J. Price and J.E. Guillet, *J. Macromol. Sci.-Chem.* **A23**(12), 1487 (1986)
26. Reference 24, Part 2 Chapter 19, p 125
27. D.S. Ballantine, R.M. White, S. Martin, A.J. Ricco, E.T. Zellers, G.C. Frye and H. Wohltjen *Acoustic Wave Sensors* Academic Press, London, 1996.
28. E.C. Baughan, *Trans. Faraday Soc*. **44**, 495 (1948)
29. N. Schuld and B.A.Wolf in *Polymer Handbook, 4th Ed* J. Brandrup, E.H. Immergut, E.A. Grulke (Eds) J. Wiley and Sons, New York, 1999. Section VII p 497
30. A. Hamdouni, J. Leonard and V.Y. Bui *Polymer Commun.* 31 258 (1990)
31. N. Schuld and B.A.Wolf *Journal of Polymer Science Part B: Polymer Physics* **39,** 651 (2001)
32. Reference 24, Part 2 Chapter 37, p 297
33. Reference 24, Part 2 Chapter 15, p 109
34. R.N. French and G.J. Koplos *Fluid Phase Equilibria* **158,** 879 (1999)

CAPTIONS FOR FIGURES

Figure 1: **Schematic Diagram of the Piezoelectric Vapour Sorption Apparatus**

Figure 2: **Response of an uncoated crystal to air or hexane vapour at 30°C**

Figure 3: **Absorption isotherms at 30°C for hexane on an uncoated crystal and a crystal coated with PDMS**

Figure 4: **Interaction parameters for solutions of PDMS at 30°C**
Closed points: this work; Open points: Reference 6.

Figure 5: **Interaction parameters for benzene and chloroform solutions with polystyrene.**
The key shows the measurement temperature in Kelvin. The lines are the best fit to measurements reported in Reference 14

Figure 6: **Temperature variation of interaction parameters for benzene and chloroform solutions with polystyrene.**

Figure 7: **Interaction parameters for solvents in polystyrene at 30°C.**

Figure 8: **Interaction parameters for solvents in poly(4-chlorostyrene) at 30°C.**

Figure 9: **Interaction parameters for solvents in PMMA at 30 °C and 40 °C.**

Figure 10: **Interaction parameters for solvents in PMMA at 30 °C and 40 °C.**

Figure 11: **Interaction parameters for n-alkyl acetates with PMMA at 30°C.**

Figure 1.

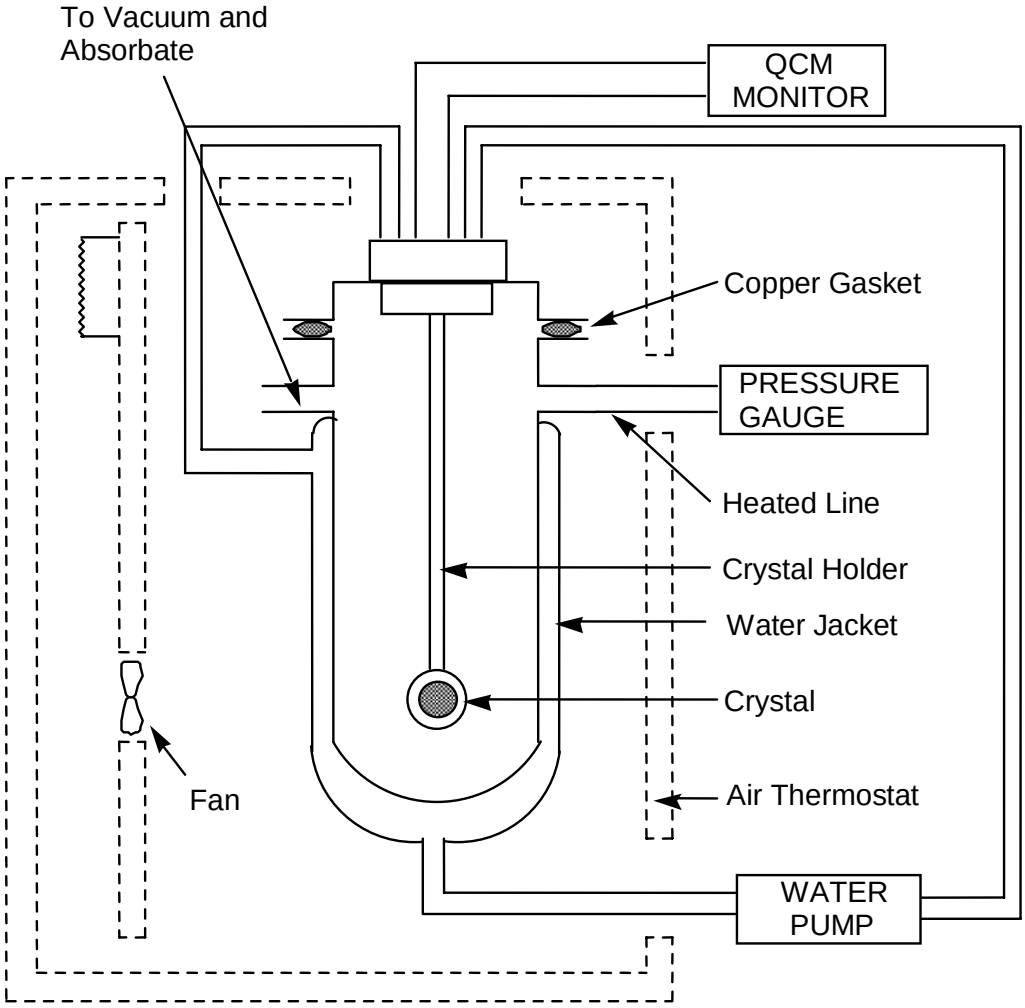

To Vacuum and
Absorbate
QCM
MONITOR
Copper Gasket
PRESSURE
GAUGE
Heated Line
Crystal Holder
Water Jacket
Crystal
Air Thermostat
Fan
WATER
PUMP

Figure 2

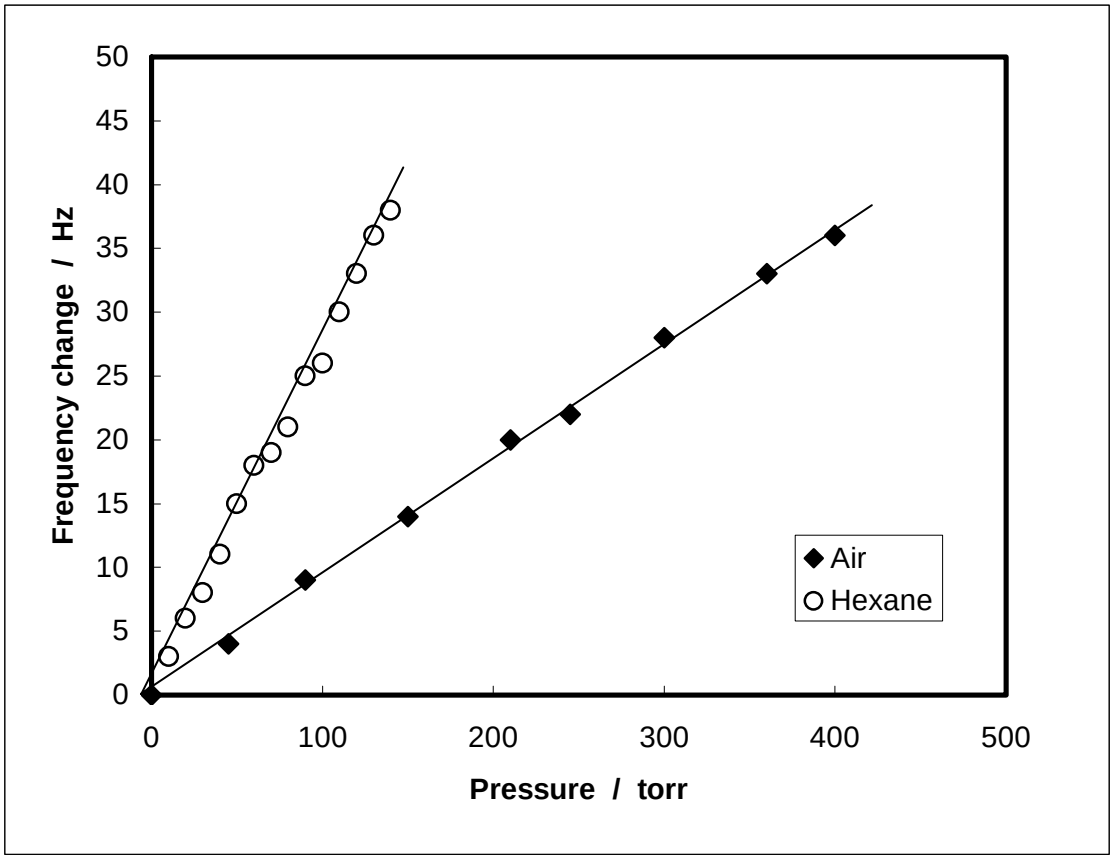

Frequency change / Hz
Pressure / torr
0
5
10
15
20
25
30
35
40
45
50
0
100
200
300
400
500
Air
Hexane

Figure 3

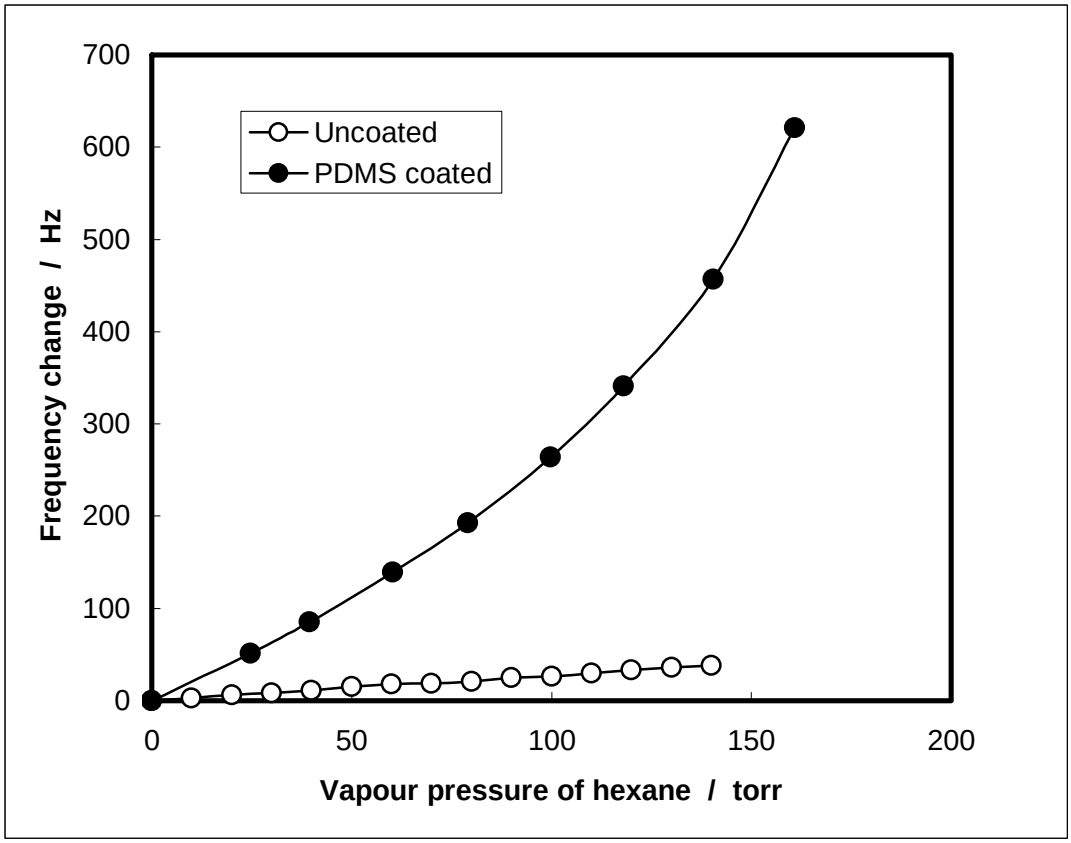

700
600
500
400
300
200
100
0
Frequency change / Hz
Uncoated
PDMS coated
0
50
100
150
200
Vapour pressure of hexane / torr

Figure 4

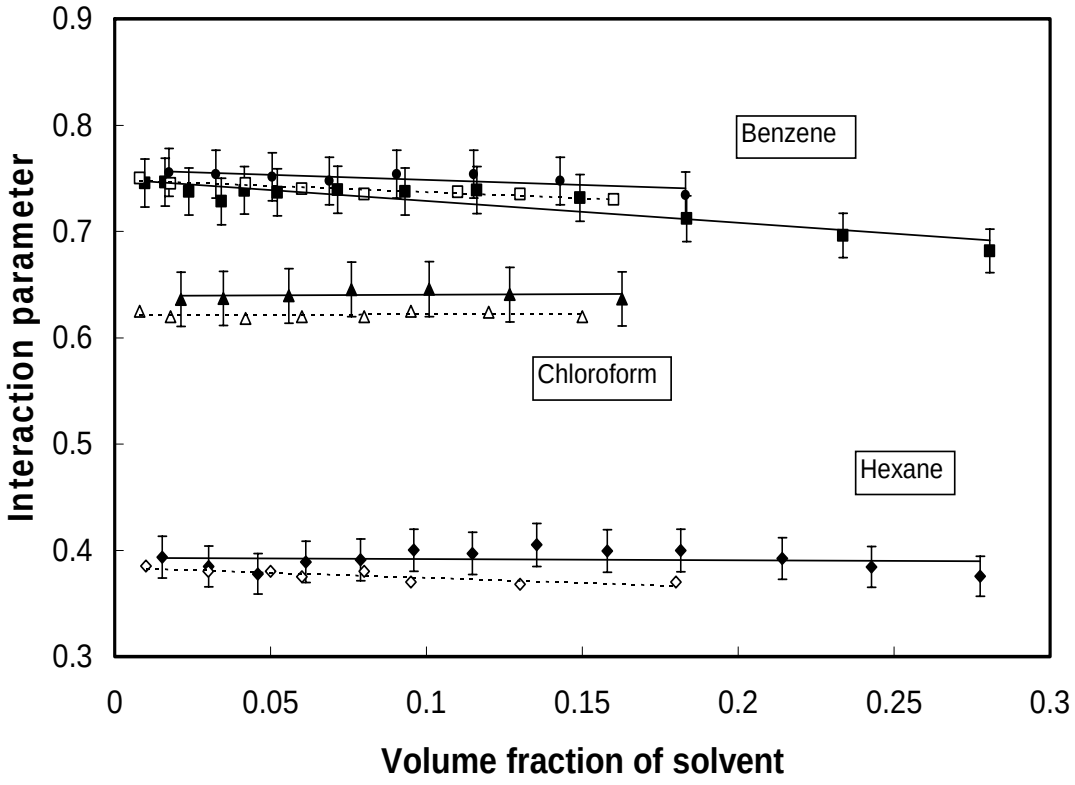

0.9
0.8
0.7
0.6
0.5
0.4
0.3
Interaction parameter
Benzene
Chloroform
Hexane
0
0.05
0.1
0.15
0.2
0.25
0.3
Volume fraction of solvent

Figure 5

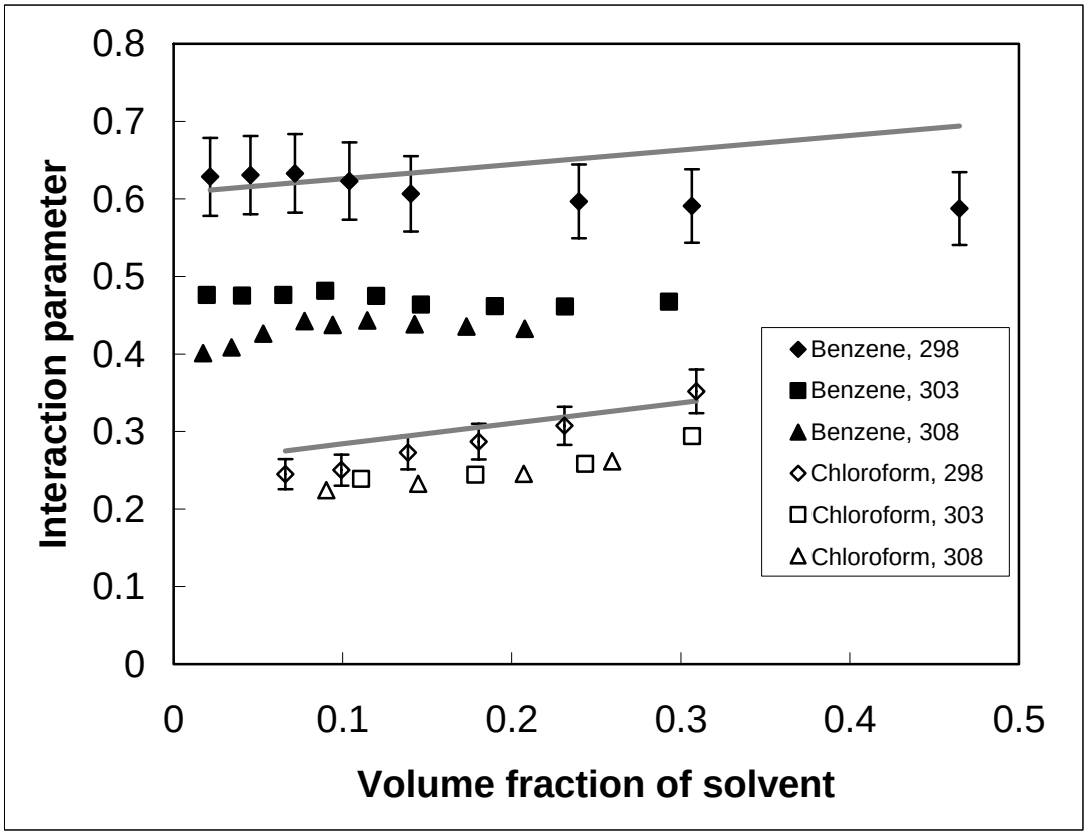

Interaction parameter
Volume fraction of solvent
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
0.1
0.2
0.3
0.4
0.5
Benzene, 298
Benzene, 303
Benzene, 308
Chloroform, 298
Chloroform, 303
Chloroform, 308

Figure 6

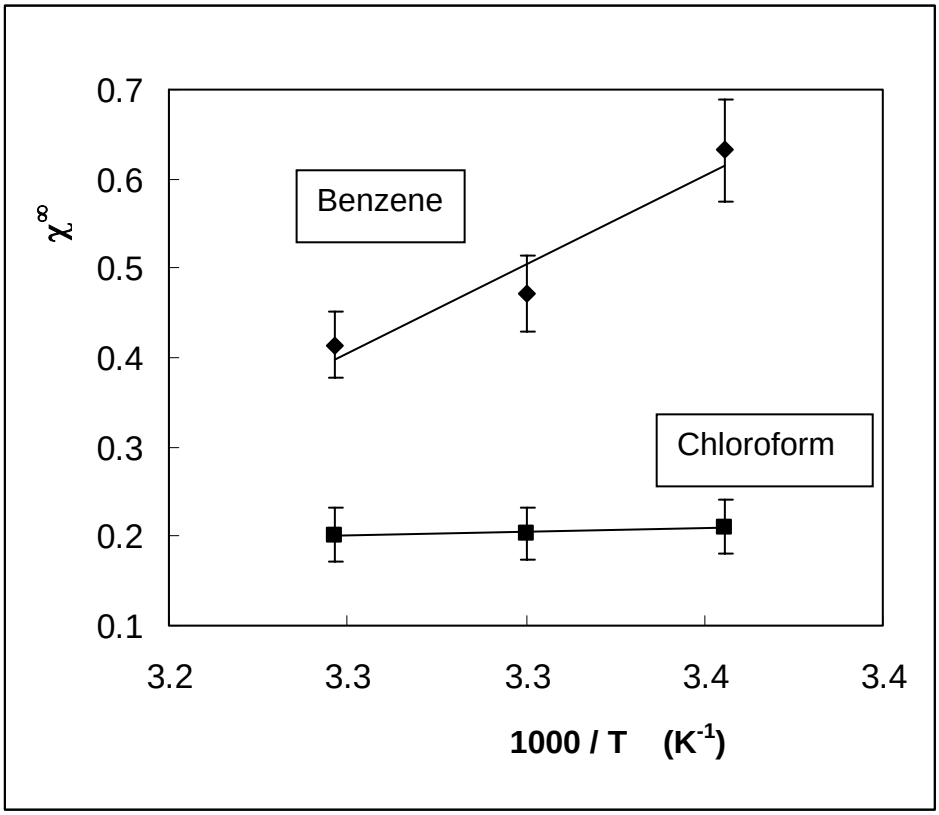

0.7
0.6
0.5
0.4
0.3
0.2
0.1
χ^{∞}
Benzene
Chloroform
3.2
3.3
3.3
3.4
3.4
1000 / T (K^{-1})

Figure 7

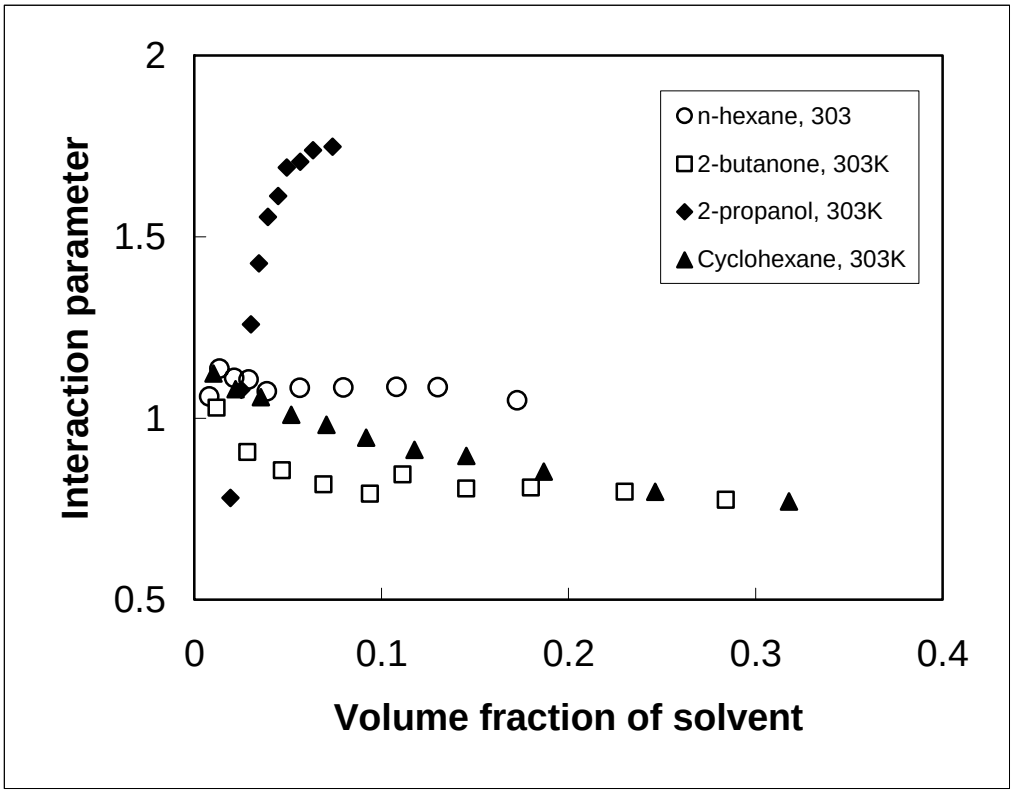

Interaction parameter
2
1.5
1
0.5
0
0.1
0.2
0.3
0.4
Volume fraction of solvent
n-hexane, 303
2-butanone, 303K
2-propanol, 303K
Cyclohexane, 303K

Figure 8

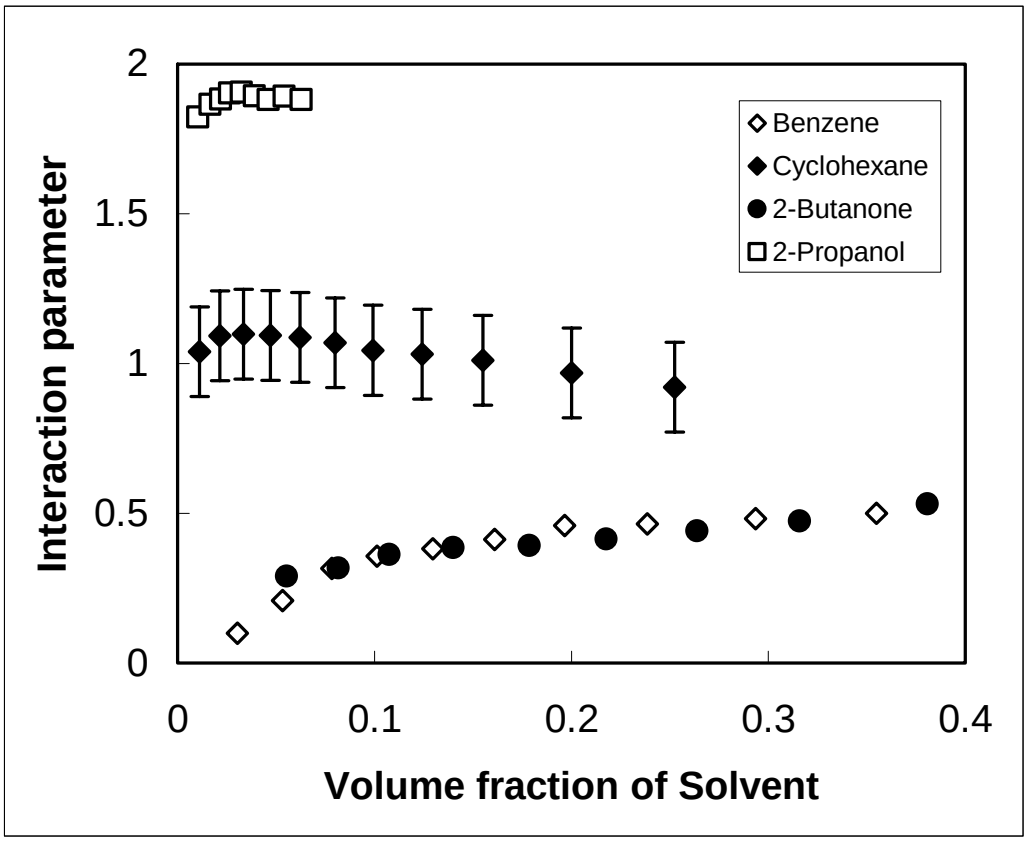

Interaction parameter
Volume fraction of Solvent
0
0.5
1
1.5
2
0
0.1
0.2
0.3
0.4
Benzene
Cyclohexane
2-Butanone
2-Propanol

Figure 9

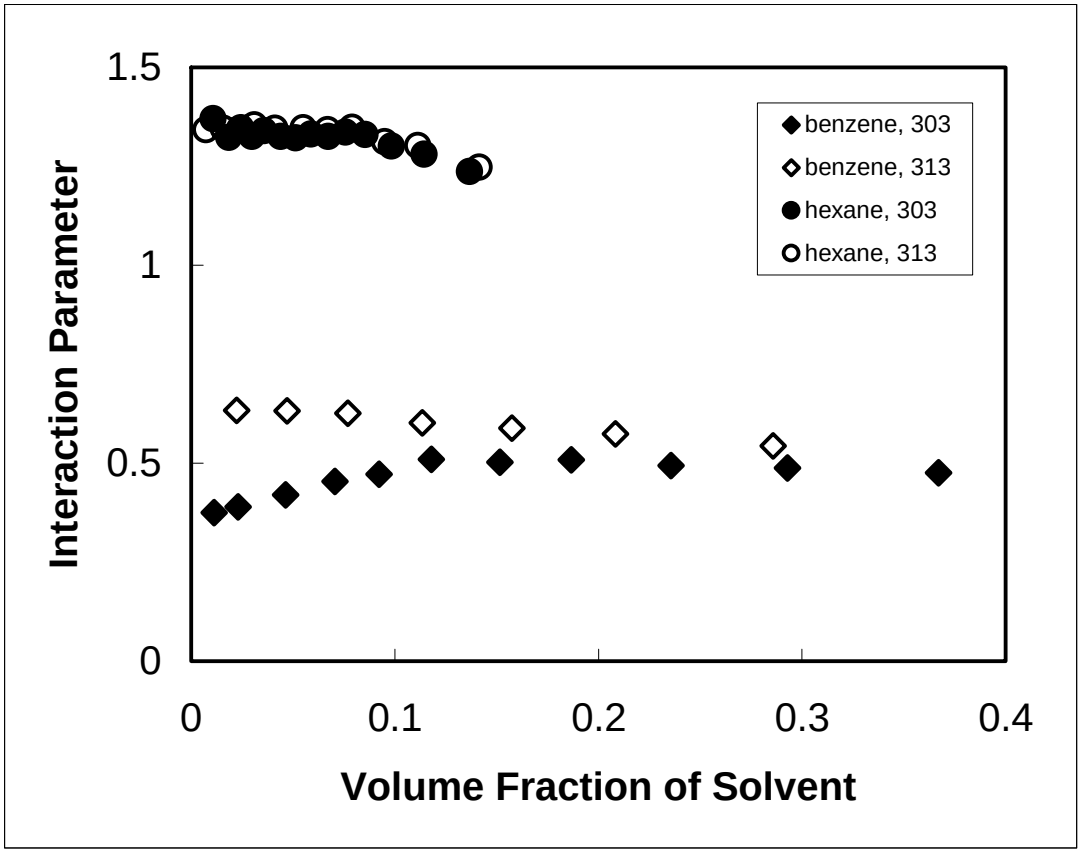

1.5
1
0.5
0
Interaction Parameter
0
0.1
0.2
0.3
0.4
Volume Fraction of Solvent
benzene, 303
benzene, 313
hexane, 303
hexane, 313

Figure 10

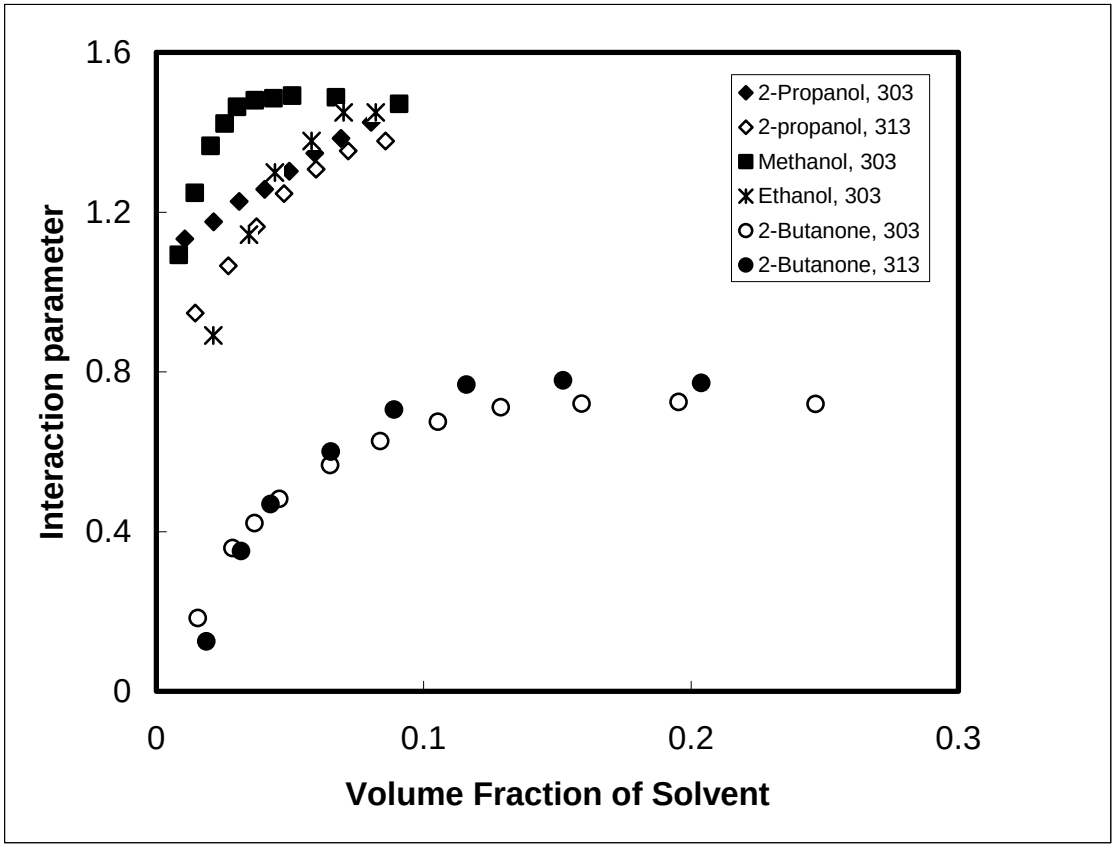
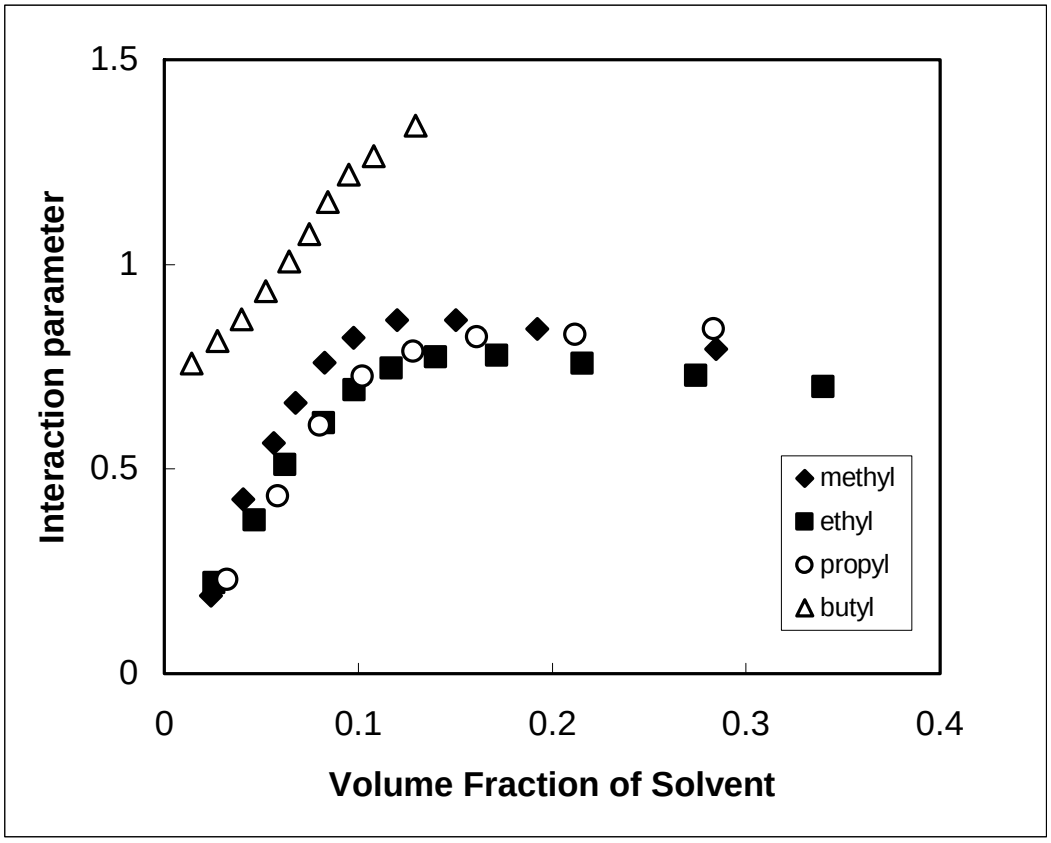

1.6
1.2
0.8
0.4
0
0
0.1
0.2
0.3
Interaction parameter
Volume Fraction of Solvent
2-Propanol, 303
2-propanol, 313
Methanol, 303
Ethanol, 303
2-Butanone, 303
2-Butanone, 313

Figure 11


1.5
1
0.5
0
Interaction parameter
0
0.1
0.2
0.3
0.4
Volume Fraction of Solvent
methyl
ethyl
propyl
butyl